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Dynamics of Bulk and Surface-Adsorbed Polyacrylates

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Introduction

The properties of a composite material depend upon the properties of each of the components and also upon the interaction of the components. These interactions take place in the interfacial region where the dissimilar materials are joined. The understanding of these interactions may be the key to the development of new composites with enhanced properties and the understanding of the properties of existing materials.

Two characteristics of the interfacial region which may be of great significance are the microstructure of the interface and the microdynamics of the molecules therein. Studies of the microstructure have yielded valuable information about composites; however, very little work has been done to characterize the microdynamics in this important region.

Nuclear magnetic resonance (NMR) spectroscopy provides a way to obtain information about the dynamics of polymers both in the bulk state and when adsorbed on a solid support, since the lineshape is dependent upon the molecular motion. The solid-state spectra of deuterated compounds are an excellent probe of molecular motion for several reasons:

1. Using a probe changes the motion of the molecule relative to a "native" molecule, i.e. one which has not been modified. The small size and mass of a single deuteron should affect the motion much less than a relatively large and bulky label such as is used in electron spin resonance spectroscopy (ESR) or photochemical studies. Additionally, the technique does not depend on the optical clarity of the samples.

2. Deuterium has a low natural abundance, so there is very little background interference from naturally occurring deuterons. A specific location on the molecule may be labelled with deuterium so that information about the motion of that part of the molecule is obtained.

3. The large quadrupolar splitting of deuterium enables a wide range of motions to be distinguished. The range encompasses approximately 5 orders of magnitude.

4. The quadrupolar splitting a given deuteron experiences is a function of the angle that the bond vector makes relative to the applied magnetic field, and is given by [1]:

$$\Delta Q = \frac{3}{4} \omega_Q (3 \cos^2 \theta - 1)$$

In this equation, ΔQ is the quadrupole splitting, ω_Q is the quadrupole coupling constant, and θ is the angle made by the bond vector and the external field. If the bond is in motion, θ will undergo time-averaging. The lineshape then depends on the effectiveness of this time-averaging in reducing the splitting.

The motion of the bond vector can be characterized by the rotational diffusion tensor, which is assumed to be symmetric about the z-axis so that it may be specified by two values: R_{xy} and R_{zz} . These values describe the rate of reorientation of the bond about their respective axes. The motion may be either a continuous rotation (which can be isotropic or anisotropic) about the diffusion axes or a series of discrete jumps [2].

Experimental

A solution of backbone methine-deuterated poly(isopropyl acrylate) (PIPA) [3] in toluene was prepared and agitated at 25 °C for 48 hours in a tube containing Cab-O-Sil grade M-5 amorphous fumed silica. The silica with adsorbed PIPA was rinsed with distilled toluene and allowed to dry at room temperature. The surface coverage is approximately a monolayer. Deuterium NMR spectra of the bulk polymer and the surface-bound polymer were then obtained at several temperatures. Deuterium NMR spectra of bulk backbone-deuterated poly(ethyl acrylate) (PEA) were also taken at several temperatures.

All spectra were taken on a Varian Associates VXR-200 NMR spectrometer at 30 MHz for deuterium equipped with the wide-line solids

accessory. The temperature was held constant to ± 0.5 °C using the Varian variable temperature controller. The solid-echo pulse technique was used with a 90° pulse width of 2 μ s. The spectral width was 2 MHz. The pulse repetition time was 1 s, and the number of echoes accumulated varied between 2000 and 16000 depending on the sample.

The experimentally obtained spectra were then simulated using the slow-motional theory developed by Freed [4]. The computer programs used were written by Schneider [5] for ESR calculations and subsequently modified by us to simulate deuterium NMR spectra. The programs run on a Silicon Graphics 4D/20 system and require from 2-10 minutes per simulation, depending on the complexity of the model.

Results and Discussion

The spectra of bulk PIPA (figure 1) show that the mobility of the polymer increases as the temperature is raised from 230 K to 290 K. One interesting feature of the bulk spectra of PIPA at the lower temperatures is the splitting evident in the central peak. This shape can be fit by assuming that anisotropic motion, in which R_{zz} is considerably faster than R_{xy} , is occurring in some segments of the molecule. Attempts to simulate the spectra using jump models yielded less satisfactory results, indicating that the molecules are undergoing continuous diffusion. The simulations provide a ratio of the contributions to the overall lineshape arising from the faster motion and the essentially rigid component. As the temperature increases, the rigid component starts to disappear and the faster motion becomes more isotropic in character.

The signal/noise ratio in the surface-adsorbed material (figure 2) is significantly lower, but the same sort of effect is seen. It is also evident that the motion of the surface-bound polymer is slower than that of the bulk polymer at both of the temperatures.

Earlier studies of PIPA using cross-polarization/magic angle spinning NMR spectroscopy [6] have shown that the carbon-13 spectra are different for the bulk and surface-adsorbed polymer. The differences were attributed to alteration of the dynamics of the polymer when attached to a surface, and the present study confirms this.

The bulk PEA spectra (figure 3) also exhibit the progressive increase in molecular motion as the temperature changes, and in addition show that there is a fairly sudden change in the shape of the spectrum which occurs between 290 and 300 K. This is significantly above the T_g (249 K [7]).

Experimental

Simulated

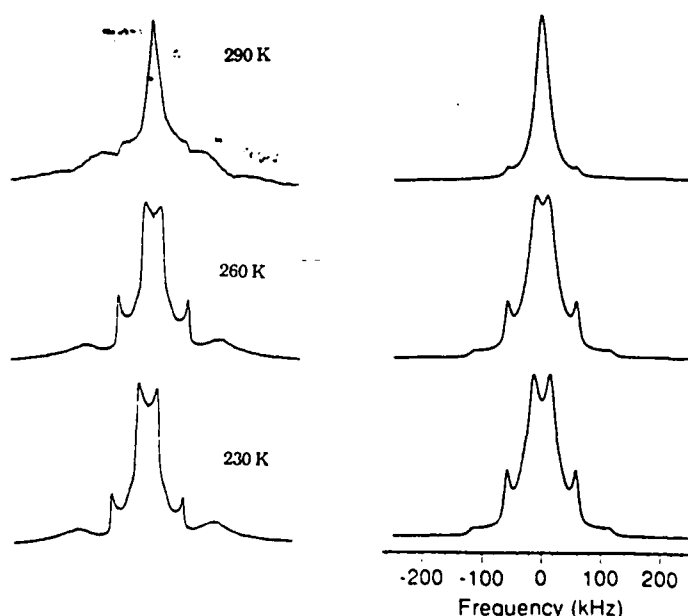


Figure 1. Experimental and simulated spectra of bulk poly(isopropyl acrylate).

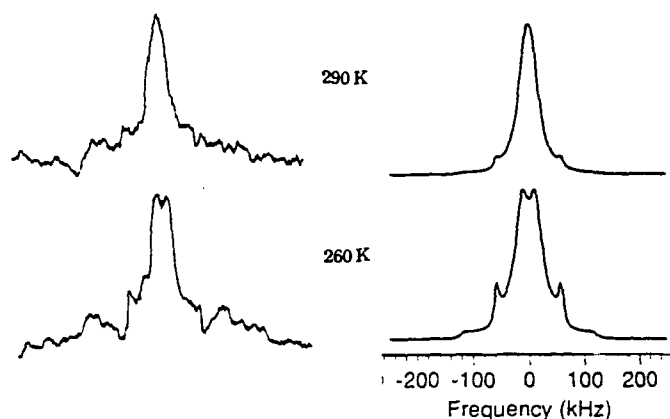


Figure 2. Experimental and simulated spectra of poly(isopropyl acrylate) adsorbed on silica.

Conclusions

The deuterium NMR spectra of poly(isopropyl acrylate) in bulk and adsorbed on a surface provide information about the dynamics of the polymer and the ways in which the presence of the surface alter those dynamics. Simulation of these spectra yields quantitative information on the relative rates of motion for the bulk and adsorbed polymer. In addition, the simulations indicate that there are qualitative as well as quantitative differences in the motion of the polymer when modified by adsorption.

The spectra of poly(ethyl acrylate) show that a sudden change in the dynamics of the material occurs around 40 °C higher than the T_g . This is due to the fact that while thermodynamic determinations of T_g are sensitive to very slow motions, the NMR experiment requires rotational diffusion rates to be on the order of 1000 s^{-1} before they significantly affect the spectra. This does not occur until the higher temperature is reached. Other studies of poly(isopropyl acrylate) [8] have shown a transition to occur in this same region.

Acknowledgements

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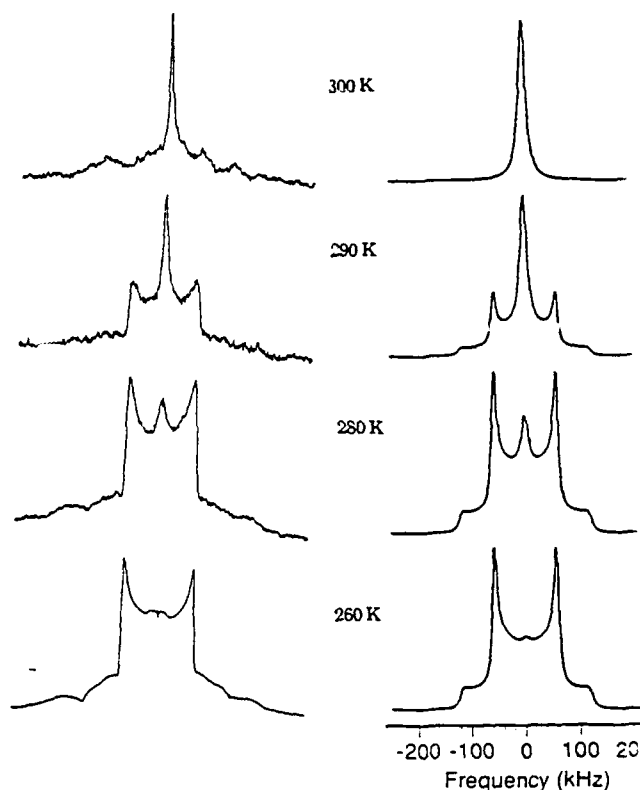


Figure 3. Experimental and simulated spectra of bulk poly(ethyl acrylate).

Table 1. Motional parameters used in the simulations

Polymer	Temp.	R_{xy}	R_{zz}	% Rigid component
PIPA-bulk	230 K	7.0×10^3	2.5×10^6	40
	260 K	1.5×10^4	2.5×10^6	35
	290 K	5.0×10^4	2.5×10^6	10
PIPA-surf.	260 K	1.3×10^4	2.0×10^6	35
	290 K	3.0×10^4	2.0×10^6	13
PEA	260 K	1.0×10^6	1.0×10^6	99
	280 K	1.0×10^6	1.0×10^6	92
	290 K	1.0×10^6	1.0×10^6	62
	300 K	1.0×10^6	1.0×10^6	0